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INVESTIGATION OF SILICATE ESTERS AS RUBBER PLASTICIZERS

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WRIGHT AIR DEVELOPMENT CENTER

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## INVESTIGATION OF SILICATE ESTERS AS RUBBER PLASTICIZERS

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*August 1952*

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Wright Air Development Center  
Air Research and Development Command  
United States Air Force  
Wright-Patterson Air Force Base, Ohio

## FOREWORD

This report was prepared by the Air Research and Development Command under the research and development project identified by Research and Development Order No. R617-12, Compounding of Elastomers. It was administered under the direction of the Materials Laboratory, Research Division, Wright Air Development Center, with Lt. D. L. Byerley acting as project engineer.

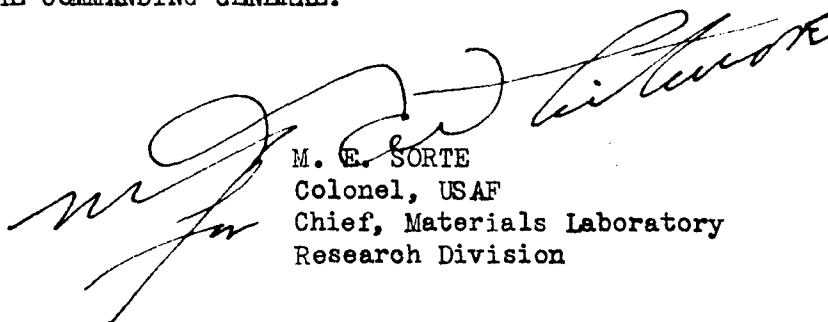
## ABSTRACT

A number of silicate esters, submitted by the John B. Pierce Foundation, Raritan, New Jersey, were evaluated as low-temperature rubber plasticizers. An attempt was also made to correlate structural variations of the esters with the properties imparted to the compounded rubber. It was found that, in general, as the ratio of the number of aliphatic carbon atoms/number of phenyl groups increased the ASTM brittle point was lowered. Variation of the structure of the silicate ester, on the other hand, appeared to have little effect on the physical properties (e.g. tensile strength, modulus, and elongation). Compatibility with common base polymers (Paracril 18, Paracril 35, and Neoprene W) decreased rather rapidly as the above ratio increased beyond a value of about 2.5. Extrapolation of these results indicates that a ratio value above 20 would not permit incorporation of a sufficient amount of the silicate ester to affect the low temperature properties of the compounded stock significantly.

## PUBLICATION REVIEW

Manuscript copy of this report has been reviewed and found satisfactory for publication.

FOR THE COMMANDING GENERAL:



M. E. SORTE  
Colonel, USAF  
Chief, Materials Laboratory  
Research Division

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## INTRODUCTION

Unplasticized rubber compounds are not, in general, flexible at temperatures much below  $-40^{\circ}\text{F}$ . An increasing urgency of requirements for better low temperature performance has necessitated an extensive continuing search for effective low temperature plasticizers. A number of silicate esters, which have not previously been studied in connection with this program, have been of interest. These were supplied by the John B. Pierce Foundation of Raritan, New Jersey and have been investigated to determine their effect on the low-temperature properties of acrylonitrile rubber. Preliminary studies indicated that these silicate esters had both relatively good viscosity-temperature relationships and low freezing points; it was therefore reasonable to expect that they would impart good low temperature flexibility to rubber if sufficiently compatible. Determination of compatibility was therefore undertaken as an essential part of this evaluation of their efficacy and permanence as low temperature plasticizers.

The results of this investigation and the trends observed are presented in this report.

## SECTION I

### COMPOUNDING METHOD

All sheet stocks were compounded on a 12-inch laboratory mill, using standard compounding procedures for each base polymer involved. The following recipe was used for determination of the effect of silicate esters on physical properties.

<u>Ingredient</u>	<u>Parts, per Hundred of Polymer</u>
Paracril 18	100
Zinc Oxide	5
Stearic Acid	1.5
Altax	1.5
Sulfur	1.5
Philblack A	60
Plasticizer	15

The compounded stocks were cured for 20 minutes at 310°F. No attempt was made to obtain optimum cures.

## SECTION II

### TESTING PROCEDURES

#### A. Compatibility

Since the amount of swell of an unplasticized stock when immersed in a plasticizer is accepted to be a satisfactory measure of the compatibility of the plasticizer with that stock <sup>1/</sup>, relative compatibility of the silicate esters with common base polymers was determined by conventional swell tests.

The tests were conducted by (1) weighing the compounded rubber specimen in air and water to determine its volume, (2) immersing the specimen in the plasticizer to be tested for 72 hours at 158°F. (70°C.), (3) again weighing the specimen in air and water after removal of the excess plasticizer, and (4) calculating the amount of swell in volume percent. All specimens were immersed and weighed under identical conditions to insure validity of results for comparative purposes. Data from the compatibility tests are presented in Appendix 1, Table II.

#### B. Rough Solubility

Although the structure of the silicate esters gave no indication of any significant insolubility in aircraft fuel, a rough solubility test was

<sup>1/</sup> Bartholomew, E. R. Investigation of Rubber Plasticizers for Low Temperature Applications. United States Air Force Technical Report No. 5891, United States Air Force, Air Materiel Command, May 1949, p. 2.



conducted inasmuch as this is of great importance where the plasticized stock is in prolonged contact with fuel. This test was accomplished by placing 3 ml of each silicate ester in a graduated cylinder, and adding enough 70/30 iso-octane/toluene blend to give a total volume of 25 ml. The mixture was then shaken, allowed to settle, and the volume of the silicate ester phase, if any, noted. It was found that all the silicate esters tested were soluble in the blend referenced above.

#### C. Physical Properties

Tensile strength, modulus, and elongation were determined in accordance with Federal Specification ZZ-R-601a. The modulus was measured at 150 percent elongation. The data for the physical properties are given in Appendix 1, Table III.

#### D. Low Temperature Properties

Three separate tests were used for determining the low-temperature properties of the plasticized stocks. These tests were: (1) brittle point, (2) bent loop, and (3) temperature-retraction.

The brittle points of the plasticized stocks were determined with a solenoid-driven brittle point tester in accordance with the procedure described in ASTM D746-44T.

Flexibility at -65°F. was determined with a cold bend test rig in accordance with ASTM D736-46T.

Temperature-retraction curves for the plasticized stocks were determined with a modified T-50 test apparatus. Specimens were stretched to 150% elongation, cooled to approximately -80°F., released, allowed to warm, and the temperatures corresponding to 5, 10, 20 ..... 80, 90, and 95 percent retraction recorded.

All the low temperature properties determined as above are tabulated in Appendix 1, Table IV.

#### E. Resilience

Bashore resilience values were determined for the plasticized stocks using a standard Bashore Resiliometer. The values obtained are given in Appendix 1, Table V.

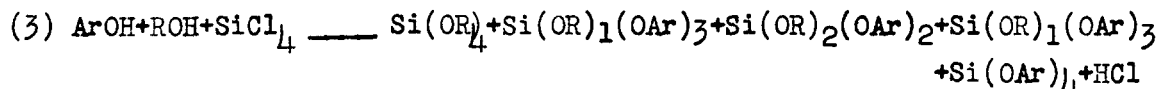
#### F. Plasticizer Volatility

The relative volatility of the silicate esters was determined by (1) weighing the samples, (2) aging the samples in a 212°F. oven for 7 days, (3) reweighing, and (4) calculating the weight loss as percent, by weight, of the

original compound. Data are presented in Appendix 1, Table IV.

## RESULTS AND DISCUSSION

The silicate esters studied were prepared as indicated by the following reactions:



The tetraphenyl silicate and tetraheptyl silicate were prepared by reactions (1) and (2) respectively. Most of the others studied, however, were prepared by reactions similar to (3); they are therefore mixtures of variously substituted silicates. The composition of this mixture may be controlled within limits, of course, by adjustment of the ArOH/ROH ratio but the formation of products other than that desired cannot be completely prevented.

Another problem encountered was the tendency of esters such as  $\text{Si(OR)}_n(\text{OAr})_{4-n}$  (where  $n = 1, 2$ , or  $3$ ) to revert on standing to an equilibrium mixture of the several different esters indicated under (3); consequently it is doubtful that isolation of any such esters of mixed composition would be of any value. Indeed the relatively constant composition of the reaction mixture is to be preferred to the changing composition of an isolated product.

Complications such as these make it difficult to obtain any very definite correlations of molecular structure, molecular weight, or oxygen content of the silicate esters with the properties imparted to the plasticized stock. However, the ratio of alkyl carbon atoms/phenyl groups for the silicate esters does appear to have some significance with respect to compatibility with the base polymers used.

It is recognized that this ratio is a measure of the molecular weight, and, in a sense, the polarity, and oxygen content of the silicate ester. As the ratio increases, the oxygen content will likely, but not necessarily, decrease because of the constant number of oxygen atoms per molecule. The oxygen content of the plasticizer molecule was considered to be a factor influencing the low temperature properties of plasticized acrylonitrile rubber in a recent study 2/. The relationship between the above ratio and compatibility with three base polymers is shown in Appendix 2, Figure 1.

2/ Hillyer, J. C. and Imig, C.S. Investigation of Plasticizers for Oil-Resistant Rubber for Service at Low Temperatures in Contact with Hydrocarbon Fluids, United States Air Force Technical Report No. 52-80, United States Air Force, Wright Air Development Center, April, 1952. p.9.

It is seen from Figure 1 that the compatibility of the silicate ester with Paracril 18, Paracril 35, and Neoprene W increases as the ratio of alkyl carbon atoms to phenyl groups decreases from 15 to about 2. It is not clear just what fine significance these curves have, but it is suggested that the polarity of the oxygen atoms is involved as a factor which assumes increasing significance as the above mentioned ratio decreases below a value of about 2. This is evidenced by the fact that the compatibility of the silicate esters with the mildly polar Neoprene W decreases somewhat below this value, whereas the compatibility with the slightly more polar Paracril 18 remains fairly constant. The compatibility of the silicate ester with the highly polar Paracril 35 continues to increase to a ratio of 1, possibly as a result of both the decreasing molecular weight and increasing polarity of the silicate ester aiding in increasing the compatibility.

It might be well to note here that all the stocks were compounded with 15 parts of silicate ester per hundred of polymer regardless of the compatibility indicated by the swell test. The incompatibility of some of the silicate esters, such as butyl polysilicate and N-amyl silicate dimer, became evident by causing the stock to be difficult to mill and by bleeding of the plasticizer from the stock after curing.

Variations in the physical properties, particularly the tensile strength, did not appear to be significant. No correlations were established between the effect of the silicate ester plasticizers on the physical properties of the compounded stock, and any characteristic of the plasticizers themselves. Observed variations in the low temperature properties of the plasticized stocks did not correspond proportionally to molecular variations in the esters. However, generally speaking, the ASTM brittle point appeared to decrease as either the size or number of the aliphatic groups increased. It will, however, be noted that increasing the aliphatic groups usually increases the molecular weight, and thereby automatically decreases the compatibility of the silicate ester. Because of such opposing, but related, variables, it is not possible to predict whether extremely low brittle points could be obtained by varying the balance between aliphatic-group size and compatibility unless further studies are made.

Temperature-retraction data on the various compounds do not seem to follow any definite pattern, and are of no apparent value except for comparison purposes.

Volatility data were obtained by the procedure described on page 3. It was found that slight variations existed in the amount of silicate ester evaporated from specimens taken from the same sheet stock. These have been attributed to varying rates of air flow through certain sections of the oven. Because of this mechanical deficiency and the presence of the before mentioned by-products, the results obtained from the volatility test are of somewhat uncertain value as far as the major component is concerned. The data are presented in this report primarily for face value; it is conceded that their interpretation may be difficult without extended studies.

In summary, it could be said that, for the most part, the physical properties remained fairly constant regardless of the silicate ester used as the plasticizer. Tensile strength, for example, did not vary significantly for any of the stocks tested at the plasticizer concentration used. Elongation and modulus did vary somewhat in a few instances, but this was thought to be due to bleeding of the plasticizer from the stock after curing, and the resultant tendency of the stock to return to the unplasticized state.

Most of the sufficiently-compatible silicate esters are satisfactory low-temperature plasticizers. In fact, they appear to be comparable to many commercial plasticizers now in use. However, in general, these esters do not appear to be quite as effective as the commercial plasticizer, Thiokol Corporation's TP-90B, which was used as a control in this study.

Incorporation of suitable groups or atoms in the silicate ester molecule might conceivably lower the volatility and impart some degree of fuel resistance to these esters. Further study along this line should be profitable.

# APPENDIX I, TABLE I

## Identification of Code Numbers

Number	Major Component	
PL8	Isopropyl triphenyl	Silicate*
PL9	Isobutyl triphenyl	"
PL13	Amyl triphenyl	"
PL14	Hexyl triphenyl	"
PL15	Isobutyl tricresyl	"
PL16	(Isobutyl), (Cresyl) <sub>0.5</sub> (3,5 Xenyl) <sub>2.5</sub>	"
PL17	Diisobutyl diphenyl	"
PL18	Triisobutyl monophenyl	"
PL19	Amyl tricresyl	"
PL20	Diamyl diphenyl	"
PL21	Triamyl monophenyl	"
PL22	Butyl polysilicate (Higher than tetramer)	
PL23	Triisobutoxy monophenyl silane	
PL24	N-amyl silicate dimer	
PL25	Tetraheptyl silicate	
PL26	Diheptyl diphenyl silicate	
PL27	Mono N-heptyl triphenyl silicate	
PL28	Tetraphenyl silicate	
TP90B	Thiokol Corporation's polyether	

\* All silicate esters were supplied by the John B. Pierce Foundation, Raritan, N.J.

# APPENDIX I. TABLE II

## Compatibility of Silicate Esters with Common Base Polymers

Plasticizer	Volume Swell, Percent, in		
	Paracril 18	Paracril 35	Neoprene W
PL8	116.3	70.4	108.2
PL9	113.4	64.6	113.9
PL13	102.7	55.1	119.1
PL14	115.8	51.0	133.6
PL15	101.4	43.9	129.4
PL16	-	25.2	-
PL17	89.3	35.3	115.2
PL18	40.9	16.2	59.1
PL19	145.1	27.1	126.2
PL20	86.4	29.1	119.6
PL21	35.8	11.5	53.5
PL22	-	1.2	1.1
PL23	45.6	-	49.4
PL24	9.1	-	9.0
PL25	8.3	-	12.4
PL26	67.1	-	74.6
PL27	112.0	-	96.6
PL28	109.6	-	79.1

# APPENDIX I, TABLE III

## Physical Properties of Plasticized Paracril 18 Stock

Plasticizer	Tensile PSI	Modulus, PSI at 150% Elong.	Elongation Percent
PL8	2080	435	340
PL9	1945	470	345
PL13	2040	450	370
PL14	1950	470	350
PL15	1935	340	400
PL16	2000	480	380
PL17	2140	460	370
PL18	1780	330	350
PL19	1920	320	415
PL20	2015	435	360
PL21	1905	305	370
PL22	2130	795	285
PL23	2290	580	355
PL24	2470	490	325
PL25	1940	335	400
PL26	1795	310	395
PL27	1820	310	410
PL28	2030	545	350
TP90B	2030	670	285

# APPENDIX I, TABLE IV

## Low Temperature Properties of Plasticized Parsoril 18 Stock

Plasticizer	Brittle Point (-°F.)	Temperature Retraction		Bent Loop Test at -65°F.
		T-0(-°F.)	T-50(-°F.)	
PL8	69	46	28	Pass
PL9	74	47	29	Pass
PL13	73	52	34	Pass
PL14	74	50	32	"
PL15	69	51	34	"
PL16	71	50	33	"
PL17	74	47	31	"
PL18	87	46	22	"
PL19	74	46	20	"
PL20	79	45	24	"
PL21	72	49	26	"
PL22	70	42	22	"
PL23	77	54	36	"
PL24	85	53	35	"
PL25	88	55	35	"
PL26	78	56	33	"
PL27	80	54	32	"
PL28	82	50	30	"
PL28*	-	51	32	-
TP90B	81	58	44	"
None	67	37	24	-

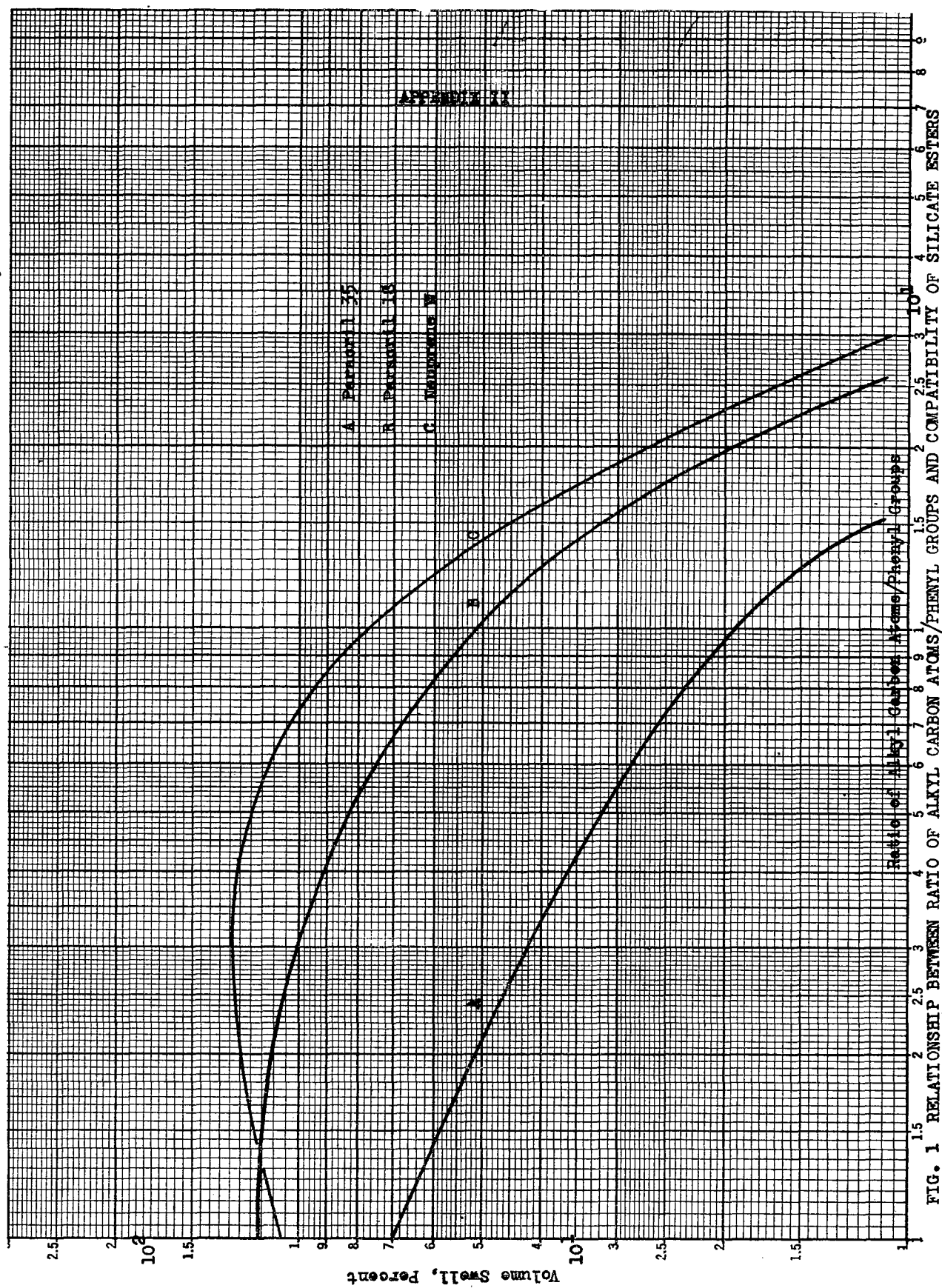
\* 40 minute cure.



# APPENDIX I, TABLE V

## Miscellaneous Data

Plasticizer	Volatility Wt. Percent of Plasticized Stock	Hardness of Plasticized Stock Shore "A"	Barshore Resilience
PL8	5.10	60	35
PL9	6.79	60-61	36
PL13	5.23	62	38
PL14	5.45	63	39
PL15	7.09	55	38
PL16	7.38	62	32
PL17	5.63	61	38
PL18	6.75	57-58	39
PL19	7.22	58	40
PL20	5.71	64	38
PL21	6.35	65	40
PL22	3.20	67	33
PL23	6.22	57	41
PL24	5.10	57	42
PL25	6.20	52	42
PL26	6.62	52	40
PL27	6.61	54	43
PL28	5.65	58	39
TP-90B	6.52	61	44



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